REPORT DOCUMENTATION PAGE			Form Approved OMB NO. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comment regarding this burden estimates or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave blan	' I		ND DATES COVERED	
4. TITLE AND SUBTITLE	8/31/96	Final Tech	nnical 7/1/95-6/30/96	
	ushajana fan Tarres		5. FUNDING NUMBERS	
A new Optical Technique for Investigating Surface Nanoscale Electron Physics			DAAH04-95-1-0383	
6. AUTHOR(S)			DAAH04-93-1-0383	
Prof. Richard M				
7. PERFORMING ORGANIZATION I	NAMES(S) AND ADDRESS(ES)	71 - Carrier Carrier Control Control		
Columbia Univer Department of E S.W. Mudd Bldg. New York, NY 1	lectrical Engineer , Rm. 1322	ing	9960910 017	
9. SPONSORING / MONITORING /	AGENCY NAME(S) AND ADDRESS(	ES)	10. SPONSORING / MONITORING AGENCY REPORT NUMBER	
U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NO	C 27709-2211		ARO 34747.1 PH-RIP	
11. SUPPLEMENTARY NOTES			-	
The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.				
12a. DISTRIBUTION / AVAILABILITY	Y STATEMENT		12 b. DISTRIBUTION CODE	
Approved for public release; distribution unlimited.			Unclassified	
13. ABSTRACT (Maximum 200 word	ds)			
This report describes the acquisition, set-up and use of essential equipment for studying surface nanoscale electronics and the progress in the related research projects where such equipment has been or will be used. During the past year, using this DURIP award, we installed a larger UHV chamber, implemented an auxiliary ultraviolet photoemission system (UPS), and established an electron-beam writing system. We have studied several nanostructured surface systems in stepped single-crystal surfaces and observed electron lateral 1D confinement and coherent effects using high-resolution angle-resolved two-photon photoemission. We investigated height-dependent (in nanoscale) electronic structures using sp-like surface state and image state electrons and observed distinct differences in the electron kinetics. We have been able to successfully generate patterns of dots and line structures of approximately 100nm in a variety of metal and semiconductor substrates.  **DTIC QUALITY INSPECT TERMS** e-beam writing, nanoscaphinement**  15. NUMBER IF PAGES**  14. SUBJECT TERMS** e-beam writing, nanoscaphinement**  15. NUMBER IF PAGES**				
14. SUBJECT TERMS e-beam writing, nanoscale patterning, stepped metal surfaces, electron confinement, angle-resolved nonlinear photoemission, surface st			ates, 7	
image states, nanoscale electronic structure				
17. SECURITY CLASSIFICATION OR REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFIC OF ABSTRACT UNCLASSIFIEI		

## **GENERAL INSTRUCTIONS FOR COMPLETING SF 298**

The Report Documentation Page (RDP) is used in announcing and cataloging reports. It is important that this information be consistent with the rest of the report, particularly the cover and title page. instructions for filling in each block of the form follow. It is important to **stay within the lines** to meet **optical scanning requirements.** 

- Block 1. Agency Use Only (Leave biank)
- **Block 2.** Report Date. Full publication date including day, month, and year, if available (e.g. 1 Jan 88). Must cite at least year.
- Block 3. Type of Report and Dates Covered. State whether report is interim, final, etc. If applicable, enter inclusive report dates (e.g. 10 Jun 87 30 Jun 88).
- **Block 4.** <u>Title and Subtitle</u>. A title is taken from the part of the report that provides the most meaningful and complete information. When a report is prepared in more than one volume, repeat the primary title, add volume number, and include subtitle for the specific volume. On classified documents enter the title classification in parentheses.
- **Block 5.** Funding Numbers. To include contract and grant numbers; may include program element number(s), project number(s), task number(s), and work unit number(s). Use the following labels:

C - Contract
G - Grant
PE - Program
Element
PR - Project
TA - Task
WU - Work Unit
Accession No.

**Block 6.** Author(s). Name(s) of person(s) responsible for writing the report, performing the research, or credited with the content of the report. If editor or compiler, this should follow the name(s).

- **Block 7.** Performing Organization Name(s) and Address(es). Self-explanatory.
- **Block 8.** Performing Organization Report Number. Enter the unique alphanumeric report number(s) assigned by the organization performing the report.
- **Block 9.** Sponsoring/Monitoring Agency Name(s) and Address(es). Self-explanatory.
- Block 10. Sponsoring/Monitoring Agency Report Number. (If known)

Block 11. <u>Supplementary Notes</u>. Enter information not included elsewhere such as; prepared in cooperation with...; Trans. of...; To be published in.... When a report is revised, include a statement whether the new report supersedes or supplements the older report.

Block 12a. <u>Distribution/Availability Statement.</u>
Denotes public availability or limitations. Cite any availability to the public. Enter additional limitations or special markings in all capitals (e.g. NORFORN, REL, ITAR).

**DOD** - See DoDD 4230.25, "Distribution Statements on Technical Documents."

DOE - See authorities.

NASA - See Handbook NHB 2200.2.

NTIS - Leave blank.

Block 12b. Distribution Code.

**DOD** - Leave blank

 Enter DOE distribution categories from the Standard Distribution for Unclassified Scientific and Technical Reports

NASA - Leave blank. NTIS - Leave blank.

**Block 13.** Abstract. Include a brief (*Maximum 200 words*) factual summary of the most significant information contained in the report.

**Plock 14.** Subject Terms. Keywords or phrases identifying major subjects in the report.

**Block 15.** <u>Number of Pages.</u> Enter the total number of pages.

**Block 16.** Price Code. Enter appropriate price code (NTIS only).

Block 17. - 19. Security Classifications. Self-explanatory. Enter U.S. Security Classification in accordance with U.S. Security Regulations (i.e., UNCLASSIFIED). If form contains classified information, stamp classification on the top and bottom of the page.

Block 20. <u>Limitation of Abstract</u>. This block must be completed to assign a limitation to the abstract. Enter either UL (unlimited) or SAR (same as report). An entry in this block is necessary if the abstract is to be limited. If blank, the abstract is assumed to be unlimited.

**DURIP Final Technical Report** 

DAAH04-95-1-0383: "A New Optical Technique for Investigating Surface

Nanoscale Electron Physics"

**Principal Investigator:** 

Richard M. Osgood, Jr., Columbia Radiation Laboratory

Our research efforts at Columbia Radiation Laboratory have been in the fields of interaction of ultraviolet laser radiation and metal/semiconductor surfaces and novel fabrication techniques for electronic and opto-electronic applications. This DURIP award allowed us to acquire essential equipment for our ongoing investigation in surface nanoscale electronics. The three main equipment sub-systems purchased using this fund are: a) UHV (ultrahigh vacuum) chamber which allows us to implement new diagnostic tools for surface electronics characterization and improve the existing system; b) Auger diagnostic system: we acquired i) a multi-technique hemispherical energy analyzer which can be used for various surface science applications, such as ultraviolet photoemission spectroscopy (UPS), x-ray photoemission spectroscopy (XPS), Auger electron spectroscopy (AES), and ion scattering spectroscopy (ISS); ii) a UPS light source, which can generate hard-UV mono-energetic photons (spectral lines from 11 to 48 eV), to attain an auxiliary (self-sufficient) UPS system for in situ analysis of surface and bulk electronic states (occupied) to provide supplementary information on the electronic structure of the surface and substrate; iii) an e-beam writing system: we purchased nanometer pattern generation system (NPGS) and accessories to convert a scanning electron microscopy (SEM) system and obtain the ability to fabricate nanoscale structures.

Our current research emphasis is to study electronic phenomena and understand quantum confinement and coherent effects at nanostructured metal surfaces using our novel nonlinear photoemission technique. The effects of surface nanostructure on electron confinement at the surface have recently attracted much attention due to the desire to engineer electronic and magnetic materials on the atomic scale. Semi-artificially, we can prepare regularly stepped surfaces with well-defined step density and orientation by the use of small-angle miscuts to the low-index single-crystal planes. Such steps are typically of nanometer height (2~3Å) and periodicity (10~30Å), and serve well as a prototype of low-dimensional (quantum wire) systems. Early studies showed markedly different electronic properties on the stepped surfaces than on flat low-index surfaces. Among them are work-function reduction, larger sticking probability for

adsorbates, and certain standing wave phenomena as detected by STM (scanning tunneling microscopy). However, these are isolated local effects and the magnitude of the electronic structure of the steps and the effectiveness of the influence of the step potential on electrons at various energy states have not been extensively studied. In our experiments, we have examined two vicinal surfaces [Cu(119) and Cu(775)]: stepped Cu(001) and Cu(111). By using various Angle-Resolved Two-Photon Photoemission (AR2PPE) techniques, we were able to probe the electronic structure as a function of distance from the surface along the surface normal and observed different electronic behaviors for the surface electrons depending on their locations with respect to the sample surface.

In initial experiments, we demonstrated the first direct observation of lateral superlattice effects for image-state electrons on stepped Cu(001) using wide-angle UV AR2PPE. Our results show that the lateral periodicity (~11Å) of the bare stepped surface leads to back-folding of the dispersion of energy versus parallel momentum, k<sub>||</sub>, of the image state. Further, adsorption of Na atoms (~0.01 monolayer) on the stepped surface enhances the step regularity and sharpens this characteristic dispersive behavior to the point that it can be followed to the edges of the lateral Brillouin zone formed by the step lattice. The reduction of the surface Brillouin zone by a factor of 4.5, compared to that of planar Cu(001), allows a clear observation of back-folding of the freeelectron-like dispersion which is normally seen on planar surfaces, yielding an oscillatory dispersive behavior where the electron energy is a multivalued function of k<sub>||</sub> as seen in the first two Brillouin zones of such a superlattice. The effects of the additional reciprocal lattice vector from the step lattice appear to have not been seen previously in the band structure of nanostructured surfaces. The results present a classic example of the 1D quantum nature that can be described by a simple Kronig-Penney model for electrons in a regular periodic potential. The fact that we observe an effect of nanostructuring on the electronic states encourages the development of artificial structures as tailored electronic materials.

In the second set of experiments, we performed comparative studies of the electronic structures (the n=0 sp-like surface state, and n=1 and 2 image states, each of which has different distances from the surface plane) on Cu(111) and stepped Cu(775) using angle-resolved resonant as well as non-resonant bichromatic or monochromatic two-photon photoemission. For Cu(775), monatomic steps are formed along  $[1\bar{1}0]$  direction and its (111) terrace consists of 7 rows of

[1 $\overline{10}$ ]-oriented atoms —giving rise to an intrinsic terrace width of  $d_0 = 14.02$ Å. By tuning the photon energy of nanosecond laser pulses, resonant bichromatic two-photon excitation from the sp surface state (n=0) to the image-potential states (n=1,2) can be achieved at various values of electron momenta parallel to the surface (k<sub>||</sub>) and hence the energy bands of both the initial and intermediate states can be mapped out simultaneously. These image states are two-dimensional in nature and the image-state electron is free-electron-like in a plane parallel to its image plane, and hence its parabolic dispersion curve is determined by the image plane orientation, i.e. the dispersion band minimum occurs at the normal of the image plane. A phase-analysis calculation shows that the n=1 image state is located about 3Å above the image plane and the n=2 imagestate electron exists about 12Å above the surface. Because of its close distance above the surface, the n=1 image-state electron can be expected to see the image plane formed on a local (111) terrace instead of the general plane of the (775) surface. In other words, the step terrace of over 10Å is large enough to support the image state. The measured dispersion data of the n=1 state agree well with this explanation: the maximum binding energy is at  $k_{\parallel} \sim 0.12 \text{ Å}^{-1}$ , which corresponds to the terrace normal [111], instead of the surface normal at  $k_{\parallel} = 0$ , revealing that the n=1 state is oriented with the step terrace not the general surface plane of Cu(775). With regard to the n=2 state, this higher Rydberg state is much further (~12Å) above the surface and thus sees the overall, averaged surface, i.e. the general Cu(775) surface, as the image plane rather than the detailed step-terrace structures. Thus, its dispersion is oriented so as to align with the Cu(775) surface not the step terrace in the [111] direction, i.e. the dispersion minimum remains at  $k_{\parallel} = 0$ . These dispersion orientations of the n=0, 1, and 2 states, can be summarized as follows: the n=2 image state senses the general surface plane, the n=1 image state senses the local terrace plane, and the n=0 surface state, which exists ~ 4 Å beneath the surface, does not appear to be affected by the steps.

Angle-resolved measurements were also done at larger  $k_{\parallel}$  values via monochromatic UV AR2PPE at different fixed photon energies on the stepped Cu(775). One important feature is that different sets of measurement at different photon energies all showed dispersion relations with a common oscillation period and thus electron bandfolding effects (such as described above for stepped Cu(001)) occurred at the same turning position despite different electron energies at the turning point. This behavior is clear evidence of Umklapp processes for the n=1 image-state

electrons in the step lattice on Cu(775), where electrons are localized ~3Å above the surface. The dispersion curves can be transformed in the k-space by the step reciprocal-lattice vector, which is of the magnitude  $0.22\text{Å}^{-1}$ . Note that such effects have not been seen by other surface electron experiments on stepped surfaces. This is another aspect that the embedded n=0 surface electron does not see the stepped structures while the n=1 image state does. The differences in the height-dependent electronic structure show that the n=1 image state is most sensitively affected by the step structure while the embedded sp surface state is not noticeably affected by the presence of steps, but rather determined only by the projection of the bulk band structure on the (775) surface.

With the new UHV chamber installed, we have been able to set up the newly acquired 100mm-radius hemispherical electrostatic energy analyzer and the differentially pumped UHVcompatible UV light source. With this UPS system in place, we have been able to obtain preliminary one-photon photoemission results on the occupied electronic states on Cu(111), Cu(775) and Si(111). We also implemented a time-of-flight (TOF) electron detector for fast, high-resolution data acquisition. Further improvement of the existing angle-resolved 160° spherical-sector energy analyzer will soon be undertaken. We have successfully converted our SEM into an electron-beam writing system with the purchase of the NPGS software and accessories. Using this device we have been able to pattern line structures, down to 130nm consistently with good control. This allows us to also make arrays of 90x120nm dots. These have been done on PMMA resist, on GaAs, Si and Al. Interestingly, we have also started patterning features that can be used to make optic devices, such as nanoscale corner mirrors. The patterns exhibited the sharpness needed for the application. These equipment additions have significantly augmented our capacity in the research activities in our current ARO- and JSEPfunded programs as mentioned above as well as a joint ARPA/AFOSR program by the principal investigator to develop novel fabrication techniques for damage-free nanostructures on semiconductor surfaces and masking techniques for optical devices. They will play a very important role in our next project investigating quantum well states and giant Magnetoresistance (GMR) in metal multilayer structures, incorporating novel techniques utilizing ultrafast laser technology.

## List of Equipment Items Acquired

	<u>Vendor</u>	Cost
1. UHV Chamber	Kurt J. Lesker Co.	\$ 8,417
<ol> <li>Auger Diagnostic System</li> <li>Hemispherical Analyzer</li> <li>Model CL100M12</li> </ol>	Micro Photonics	\$ 58,874
b) UPS Light Source Model UVL-HI	Kurt J. Lesker Co.	\$ 10,018
c) UV Film Polarizer Model TFK2-266-60	CVI Corp.	\$ 1,815
<ul><li>3. E-beam Writing System</li><li>a) Nanometer Pattern</li><li>Generation System</li></ul>	JC Nabity Lithography System	\$ 22,000
b) SEM Conversion Accessories	Omicron Associates First Source Int'l.	\$ 1,295 \$ 203
TOTAL		\$102,622